# PRODUCTION OF SILICON SINGLE CRYSTAL AND SILICON SILIC

Patent Number: JP11199387
Publication date: 1999-07-27

Inventor(s): YAMANAKA HIDEKI; SAKURADA MASAHIRO; HORIE SHINICHI

Applicant(s):: SHIN ETSU HANDOTAI CO LTD

Requested Patent: JP11199387

Application Number: JP19980021410 19980119

Priority Number(s):

IPC Classification: C30B29/06; C30B15/20

EC Classification:

Equivalents:

#### **Abstract**

PROBLEM TO BE SOLVED: To provide a method for producing a high-quality silicon single crystal having no growth defect in the whole region of wafer and slight variation of precipitated amount of oxygen by pulling up the crystal while controlling a pulling up speed being a variable having both commonality and generality and to obtain the silicon single crystal produced by the method.

SOLUTION: In a method for growing a silicon single crystal by a czochralski method, a crystal pulling up speed is controlled to grow the crystal while controlling the speed between a transition pulling up speed Pc at which a transition from a zone in which an atomic vacancy is excessive but no growth defect exists to a zone in which an interstitial silicon atom is excessive but no its aggregate exists occurs and a transition pulling up speed Pi at which a transition from a zone in which an interstitial silicon atom is excessive but no its aggregate exists to a zone in which the aggregate of the interstitial silicon atom exists occurs. The silicon single crystal is obtained by the method. A silicon single crystal wafer is obtained from the silicon single crystal.

Data supplied from the esp@cenet database - I2



## MACHINE-ASSISTED TRANSLATION (MAT):

(19)[ISSUING COUNTRY]

Japanese Patent Office (JP)

(12)
Laid-open (kokai) patent application number (A)

(43)[DATE OF FIRST PUBLICATION]
July 27th, Heisei 11 (1999)

(54) [TITLE]

The production of a silicon single crystal and the silicon-single-crystal wafer

(51) (51)[IPC]
C30B 29/06 502 C30B 29/06 502
15/20 15/20

[FI]
C30B 29/06 502 J
C30B 29/06 502 J
15/20
15/20

[EXAMINATION REQUEST]
UNREQUESTED

[NUMBER OF CLAIMS] Nine

[Application form] FD

[NUMBER OF PAGES] 13



(21)[APPLICATION NUMBER] (21) Unexamined Japanese patent 10-21410 (22)[DATE OF FILING] (22) January 19th, Heisei 10 (1998) (71)[PATENTEE/ASSIGNEE] (71) [ID CODE] 000190149 Shinetsu semiconductor K.K. [ADDRESS] (72)[INVENTOR] (72) Hideki Yamanaka [ADDRESS] (72)[INVENTOR] (72) Masahiro Sakurada [ADDRESS] (72)[INVENTOR] (72)



Shinichi Horie

[ADDRESS]

(74)

(74)[PATENT AGENT]

[PATENT ATTORNEY]

Mikio Yoshimiya

(57)

(57)[SUMMARY] (Amended)

[SUBJECT]

P

To provide a method for producing a high quality silicon single crystal having no growth defect in the whole region of wafer and slight variation of precipitated amount of oxygen by pulling up the crystal, controlling a pulling-up speed P which is a variable having commonality and generality, and the silicon single crystal produced by the method.

#### [SOLUTION]

PcPi

Production of the silicon single crystal characterized by that the crystal is grown, controlling a crystal pulling-up speed between a transition pulling-up speed Pc at which a transition from a zone where an atomic vacancy is excessive nut no growth defect exists to a zone where an interstitial silicon atom is excessive but no its aggregate exists occurs, and a transition pulling-up speed Pi at



which a transition from a zone where an interstitial silicon atom is excessive but no its aggregate exists to a zone where the aggregate of the interstitial silicon atom exists occurs, in growing a silicon single crystal by the Czochralski method.

And, the silicon single crystal obtained by this method, and silicon-single-crystal wafer.

#### [CLAIMS]

#### [CLAIM 1]

Production of the silicon single crystal characterized by that the crystal is grown in a zone in which an interstitial silicon atom is excessive but no aggregate exists in growing a silicon single crystal by the Czochralski method.

#### [CLAIM 2]

Production of the silicon single crystal characterized by that a crystal is grown, controlling a crystal pulling-up speed between a transition pulling-up speed Pc at which a transition from a zone where which an atomic vacancy is excessive but no growth defect exists to a zone where an interstitial silicon atom is excessive but not aggregate exists occurs and a transition pulling-up speed Pi at which a transition from the zone where an interstitial silicon atom is excessive but no aggregate exists to a zone where aggregate of the interstitial silicon atom exists occurs, in growing a silicon single crystal by the Czochralski method.

PcPi



Pc.minPi.max

#### [CLAIM 3]

When a transition point from a zone where an atomic vacancy is excessive but no growth defect exists to a zone where an interstitial silicon atom is excessive but no aggregate exists varies based on the radial direction of a crystal, a crystal is grown, controlling the crystal pulling-up speed between the smallest transition pulling-up speed (Pc.min) in the transition pulling-up speeds corresponding to the transition point, and the largest transition pulling-up speed (Pi.max) in the transition pulling-up speeds corresponding to transition point to a zone where the aggregate of an interstitial silicon atom exists from a zone where an interstitial silicon atom is excessive but no aggregate exists.

Production of a silicon single crystal described in Claim 2 characterized by the above-mentioned.

#### [CLAIM 4]

When a transition point from a zone where an atomic vacancy is excessive but no growth defect exists to a zone where an interstitial silicon atom is excessive but no aggregate exists varies based on the radial direction of a crystal, the proportion based on Pc.min of the difference between the largest transition pulling-up speed (Pc.max) in the transition pulling-up speeds corresponding to the transition point and the smallest transition pulling-up speed (Pc.min) is made 0% - 7%.

Production of a silicon single crystal described in Claim 2 or Claim 3 characterized by the

Pc.maxPc.minPc.min



above-mentioned.

## G GmaxGminGmin20

#### [CLAIM 5]

The proportion based on Gmin of the difference of the maximum Gmax in the radial direction of crystal growth temperature-gradient-in-axial-direction G of just overhead of the boundary-surface between silicon melt solution and crystal, and the minimum-value Gmin is made 20% or less.

Production of a silicon single crystal described in any one of Claims 2 - Claim 4 characterized by the above-mentioned.

#### [CLAIM 6]

PcPiPc.maxPc.minPi.max

In the production of a silicon single crystal described in any one of Claim 2 - Claim 5, the above-mentioned Pc and Pi, Pc.max and Pc.min, and Pi.max are determined as follows.

The crystal is grown, reducing a pulling-up speed gradually during the drawing of a single crystal performed beforehand.

The sample which is cut longitudinally in parallel with the crystal growth axial direction through the crystal center shaft is cut out from the grown single-crystal rod. An etching process is performed in order to remove a surface process distortion. The deposition of oxygen and heat treatment is performed to this, and the distribution of the defect is found in the sample. Or the lifetime of a small amount of carrier is measured and the distribution of the lifetime is found in the sample.

Production of the silicon single crystal characterized by the above-mentioned.



#### [CLAIM 7]

The silicon single crystal produced by the production indicated in Claim 1 - Claim 6.

#### [CLAIM 8]

The silicon-single-crystal wafer obtained from the silicon single crystal produced by the production indicated in Claim 1 - Claim 6.

#### [CLAIM 9]

It is the silicon-single-crystal wafer grown by a Czochralski method.

In the whole region of wafer, an interstitial silicon atom is contained excessively.

The abnormal oxygen precipitate zone resulting from excessive atomic vacancy is not included. The silicon-single-crystal wafer which does not contain the growth defect which is the aggregate of an atomic vacancy, and the aggregate of an interstitial silicon atom, and the crystal defect to be used as the nucleus of the oxidation induction lamination defect formed when performing a thermal-oxidation process.

#### [DETAILED DESCRIPTION OF INVENTION]

[0001]

### [TECHNICAL FIELD]

This invention relates to the production of a silicon single crystal which are used for manufacture of a semiconductor-integrated-circuit element etc. and the silicon-single-crystal wafer.



#### [0002]

#### [PRIOR ART]

1420200mm mm/min1000OSF OSF 0.401.5 The silicon-single-crystal wafer used as a substrate of a semiconductor-integrated-circuit element is mainly produced by the Czochralski method (CZ process).

The CZ process is the method of growing a cylinder shaped silicon single crystal by immersing a seed crystal of a silicon single crystal in the silicon melt solution which is melted at a high temperature of 1420 degrees C or more in a quartz crucible, and by pulling up a seed crystal gradually, rotating a quartz crucible and a seed crystal.

Generally, the bigger the diameter of the growing crystal becomes, the bigger the solidification latent heat to be released becomes when the melt solution solidifies. Consequently, the pulling-up speed needs to be made small.

For example, generally, the pulling-up speed of a crystal with a diameter of 200 mm is 0.40-1.5 mm/min.

If a high-temperature thermal-oxidation process of 1000 degrees C or more is performed to the wafer produced from the silicon single crystal thus produced, the oxidation induction lamination defect (it describes as a ring OSF nearly hereafter) called OSF may be formed in a ring shape on a wafer.

[0003]



Defect) Tomograph Negative crystal

OSF 4-192345FPD Flow Pattern However, as for the silicon-single-crystal wafer Defect COP Crystal Originated produced at a comparatively high pulling-up Particle LSTD(Laser Scattering speed, a ring OSF is left off to the outside of Void, the wafer or exists in the most outer periphery of a wafer.

> Inside a wafer, the atomic vacancy which is lattice points where a silicon atom is missing, is excessively received on the solid-liquid boundary surface.

> It aggregates during crystal cooling and it grows to be an observeable defect.

This is called growth defect.

Fusegawa, et al. (Japanese Patent Laid-open No. 4-192345) showed for the first time that this growth defect is observeable by the seco etching liquid which corrodes the defect selectively.

This is called FPD (Flow Pattern Defect).

Then, the detection by another method is examined. The defects called COP (Crystal Particle) and LSTD Originated Scattering Tomograph Defect) also appear.

However, the latest study made it clear that these are an identical entity.

That electron-microscope is, by the observation, it is analyzed that it is the cavity (called Void or Negative crystal) of a regular octahedron atomic that the vacancy aggregated.

#### [0004]

0.2 m 1 m 1 m

The size of this growth defect is as big as 0.2 m.

It hardly influenced on the yield of a device in the age that the degree of integration of a device is small and design rules are 1 m or



more.

However, when it became 1 m or less, it became clear to have a bad influence on a device.

If a growth defect exists in the inside of or the vicinity of the device activated layer, poor joining leak will be caused.

If it exists on the wafer surface, a poor oxidefilm withstand-pressure and poor joining leak will be caused.

From now on, since the degree of integration of a device becomes still large, it will be required to reduce the density and the size of this growth defect, or extinguish it, and furthermore not to form it.

#### [0005]

As the trial which does not form the growth defect resulting from this atomic-vacancy, the development and trial production of the so-called low-speed pulling-up crystal which made the ring OSF in a wafer periphery contract into the wafer (crystal) center section performed around 1990.

For the crystal manufacturer, it was well known as experiential findings, that the smaller pulling-up speed is made, the smaller the diameter of a ring of a ring OSF becomes, and that when setting at a certain pulling-up speed or less, it is contracted in the crystal centre.

However, because the problems that since OSF formed on the surface becomes the largest, the device formed on the surface is affected, and that the productivity of the crystal is reduced by making the pulling up speed low, the manufacture of the wafer by low-speed-

OSF 1990OSF OSF



izing pulling-up speed was avoided.

#### [0006]

271990W.V.Ammon of Crystal Growth vol.151, physics No. 60, p.766, 1991). Growth, vol. 59, p. 625, 1982

OSF 60p 766 1991OSF 7 p In such a situation, Shinoyama et al. released OSF as reference that when pulling-up speed is Pcrit(mm/min) G /mm Pcrit/G = made small, a ring OSF will contract and 0.13 mm<sup>2</sup>/ min 7-257991Journal disappear in the crystal centre (The Applied

p.273-277, 1995 P/G V. V. Moreover, Tachimori et al. announced that a Voronkov: Journal of Crystal defect did not occur on the outer side, although the poor oxide-film withstand-pressure occurred at the inner side of the wafer where a ring OSF exists. (The Applied Physics Society Crystal Engineering subcommittee, the 7th crystal engineering symposium, p.27, 1990).

> The development of a low-speed pulling-up crystal and trial production came to be performed triggered by this announcement.

> As a result, W. V. Ammon et al. proved experimentally and announced that a pullingup-speed Pcrit (mm/min) at which a ring OSF contracts to the crystal centre is proportional to crystal side center temperature-gradient G (degree C/mm) of a growth axial direction, and is imparted with Pcrit/G=0.13 mm2/degree (Japanese Patent Laid-open No. 7-C\*min 257991, or Journal of Crystal Growth vol. 151, p.273-277, 1995).

> This was the first work which showed experimentally the theory advocated by V. V.Voronkov, i.e., the theory that the kind and the density of excessive point defects are determined by P/G (Journal of Crystal Growth, vol.59, p.625, 1982).

[0007]



Etch PitLEP LEP

OSF OSF OSF FPD Large However, crystal manufacturers knew that the selective-etching pit whose size and shape are completely different from FPD which is a growth defect resulting from an atomic vacancy, is observed at the outer side of a ring OSF, or on the wafer where the ring OSF contract and disappear (since this is the same as the wafer where the outer side of a ring OSF widened on the whole, it names the outer side of a ring OSF generically hereafter).

> Since it did not influence on an oxide-film withstand-pressure, they did not matter at the early stage.

> However, it becomes clear that the defect who originated in leak was generated in the device yield.

> The wafer where no crystal defect (henceforth, the crystal defect is also described as LEP) exists which will cause this big selectiveetching pit (It calls as Large Etch Pit, and describes LEP here; a interstitial transition loop, the transition cluster, and large dislocation may be called.) is needed.

#### [8000]

OSF OSF FPD LEP FZLEP

Thus it became clear that a crystal defect of a different kind is completely formed, with the zone of a ring OSF as the boundary.

At present, as mentioned above, it is clear that FPD which is a growth defect inside a ring OSF is the cavity where the atomic vacancy aggregated.

However, the entity about the LEP which exists at a low density outwardly is not yet clarified.

From the contrast with the research result of



the crystal defect in a floating zone method (FZ method), it is estimated that LEP will be the aggregate of an interstitial silicon atom and will be the transition loop and its cluster.

Since this is also formed during crystal cooling, it is a growth defect.

#### [0009]

FPD LEP OSF

According circumstances. to such the development of the wafer which no FPD, LEP, and ring OSF exist, became important and indispensable subject for the crystal manufacturer.

#### [0010]

**Progress** in Fablication, 1993 Technical LEP OSF FPD LEP

FPD LEP OSF M Hourai et al.: On the one hand, from Horai et al. released the Semiconductor data which suggest possibility of a wafer that SEMICON/Europe, no FPD, LEP, and the ring OSF exist. Conference, (M.Hourai et al.:Progress in Semiconductor Geneva, March/April, 1993 4 OSF Fablication, SEMICON/Europe, 1993 Technical Conference, Geneva, March March/April, 1993).

The data is shown in Diagram 1.

This is the sketch diagram of about quarter of the wafer which carried out the thermodiffusion of copper from the wafer surface, was made to ornament a crystal defect, and performed X-ray topograph photography.

It turns out that there is a zone where no crystal defect exists between a ring OSF zone and LEP (transition loop and its cluster) zone. That is, it suggested that the zone where no FPD, LEP (transition cluster) exist at the outside of a ring OSF was formed, and the zone could be further enlarged according to the crystal growth conditions.



#### [0011]

OSF 8-330316P mm/min1300G /mm P/G 0.200.22mm<sup>2</sup>/ min

Then, by Horai et al., it is silicon-single-crystal wafer grown by the Czochralski method, and is a low-speed growth wafer in which the oxidation induction lamination defect (ring OSF) which develops with a ring shape when carrying out a thermal-oxidation process disappeared in the wafer center section.

And the transition cluster is eliminated from the wafer whole surface.

The silicon-single-crystal wafer characterized the above-mentioned by invented was (Japanese Patent Laid-open No. 8-330316).

Furthermore, it proposed that such a wafer was realizable by controlling the value of P/G to 0.20-0.22 mm2/degree C\*min when setting pulling-up speed at P (mm/min), and the mean value of the temperature gradient of the pullingup axial direction from the melting point of a silicon to 1300 degrees C at G (degree C/mm).

#### [0012]

Pcrit/G Vol.24, No.4, P22, 1997 Pcrit/G

P/G 0.22 mm<sup>2</sup>/ min OSF 1 7 In it, when P/G serves as 0.22 mm<sup>2</sup>/degree 0.15 mm<sup>2</sup>/ min C\*min, the ring OSF is presupposed to contract to an in-crystal centre.

> This is larger 1.7 increment compared with the above-mentioned value such as von \*Ammon.

> Moreover, in the announcement by Nakamura et al., it is Pcrit/G=0.15 mm2/degree C\*min (the Japanese crystal growth congress report, Vol.24, No.4, P22, 1997).

> The value of Pcrit/G thus depends on greatly with the announcement organization.

[0013]



1993OSF FPD

It is not clear whether the wafer proposed by Horai et al., is realizable.

However, as stated above when seeing the photography (see Diagram 1) announced officially in 1993, it is a fact that there is actually a zone where no transition cluster nor FPD exists at the outside of a ring OSF.

#### [0014]

The above content is the latest technical situation of the reduction and elimination of a growth defect resulting from an atomic vacancy and an interstitial silicon atom.

However, the crystal defect which has important influence on a device in a silicon single crystal by the CZ process conventionally is oxygen deposit.

The control technique is an important technique in a device process.

In recent years, the device thermal process has low-temperature-ized.

The control of the density of the oxygen deposit is more important.

#### [0015]

Since a quartz crucible is used in a CZ process, oxygen melts into a silicon melt solution from a quartz crucible, and is received in crystal receives.

And, it becomes supersaturation during crystal cooling.

Aggregation of oxygen occurs.

Aggregation is most promoted in the vicinity of 650 degrees C and 500 degree C.

Therefore, since the nucleation of this oxygen deposit occurs in response to the heat history

CZ

CZ650 500



of the low temperature under crystal cooling, the density of an oxygen precipitate nucleus of the upper part of a crystal differs greatly from that of the lower part.

Of course, an oxygen precipitate nucleus density depends on the supersaturation oxygen concentration received in the crystal.

The higher the concentration is, the more it increases.

Therefore, the precision control of the supersaturation oxygen concentration is required by the wafer manufacturer.

#### [0016]

As for the oxygen precipitate nucleus formed during crystal manufacture, supersaturation oxygen precipitates in those nucli in a subsequent device thermal process to grows to be a bigger oxygen deposit.

Oxygen deposit has the important role of gettering heavy metal which contaminates from the outside such as an apparatus, in a device manufacture process.

On the one side, when deposit is formed with a high density, it exists even in the inside of a device activated layer, or its vicinity, and it causes poor joining leak

In the conventional thermal process, there is a high-temperature process of 1200 degrees C in a comparatively early phase of the entire heat processing.

The remarkable amount of the oxygen precipitate nucleus formed during crystal manufacture is dissolved again.

The difference in the density of the oxygen precipitate nucleus potentially contained in the

120010001050



wafer between wafers, in other words crystals or crystal positions was eliminated.

However, recently, the early heat treating is low-temperature-ized.

It is 1000-1050 degrees C.

It is the process that the oxygen precipitate nucleus formed during crystal manufacture grows as it is, without dissolving.

For this reason the control of the density of the oxygen precipitate nucleus under crystal manufacture is considered importantly more than conventional.

Therefore, the method of suppressing variation in the density of the oxygen precipitate nucleus between the wafers which occurs during crystal manufacture needs to be invented.

[0017]

#### [PROBLEM ADDRESSED]

**FPD** 

OSF OSF OSF LEP OSF LEP As mentioned above, it is a well-known fact for the persons engaged in crystal manufacture in the crystal manufacture manufacturer that when the pulling-up speed is made small, the path of a ring OSF will become small, and contract and disappear in the crystal centre at a certain pulling-up speed.

> Moreover, it is also a fact that the cavity which is the aggregate of an atomic vacancy is formed inside a ring OSF as a growth defect.

> Moreover, as Horai et al. announced officially, it is also well-known that LEP (the transition loop and its cluster) which is the aggregate of an interstitial silicon atom is formed at the outer



side of a ring OSF.

Moreover, Horai et al. developed the findings that a zone where no growth defect FPD exists between the ring OSF circumference part and the LEP zone of its outer side.

They proposed extending the zone throughout a wafer.

#### [0018]

P/G G OSF Pcrit/G G FEMAG F. Transfer, vol. 33, p. 1849, 1990 G

In the invention of Horai et al., the method to Dupret et al; Journal of Heat extend a defect-free zone to a wafer whole surface or a crystal full length is specified in the range of P/G.

> However, since the value of G is not the value at the time of actual crystal growth but based on the comprehensive heat-transfer analysis simulation, it does not become the value which has the generality among crystal manufacture manufacturers.

> As mentioned above, that is supported by the fact that the value of Pcrit/G by which a ring OSF contracts to the crystal centre is the value which depends on the organization.

> The value of G depends on which simulation software developed in each organization, or commercially available simulation software (for example, software called FEMAG:F.Dupret et al; Journal of Heat Transfer, vol. 33, p. 1849, 1990) is used.

> Furthermore, G will become the value which depends on the method of creation of a finiteelement mesh, boundary conditions, and the method of a definition of the gradient.

#### [0019]

P/G G G

Therefore, the value of P/G is not suitable as a



variable which is provided with generality and commonality and is controlled.

Generally, the value of G is not the variable controlled in crystal growth but a parameter which is imparted to the designed heat-retention structure in the furnace.

It is very hard to modify and control this in pulling up the crystal.

Moreover, its absolute value does not have commonality and generality either, the value of G calculated by simulation should be used as relative value within each organization.

On the other hand, the pulling-up speed is a variable common to any organization.

Since it is actually controlled, it is suitable as a variable.

#### [0020]

On the one hand, there is not still a theory or an experiment fact which completely contradicts the theory of Voronkov that the kind and amount of excessive point defects are determined by P/G.

However, it is not the theory which provides the critical value at which the transition of the kind of point defect occurs, as a concrete numerical value. It is not the theory which provides the numerical value of P/G at which the growth defect which is the aggregate of a point defect is formed, either.

Moreover, it is very difficult to prove that transition is carried out at the same P/G to every heat-retention structure in the furnace, even though the experimental result that the transition point is determined only by the value of P/G is obtained.

P/G P/G P/G P/G G



Because it is since the value of G depends on the analysing organization, there are not commonality and generality.

#### [0021]

From such a situation, if the general method of determining the boundary between the formation zone of a growth defect and a defect-free zone not by P/G but by pulling-up-speed P which is an actual control variable can be discovered, it is very effective in actual crystal manufacture.

Since it is the general method, it has the commonality between each organization, and becomes a simple and very practical method.

#### [0022]

On the one hand, as mentioned above, Horai et al. developed the findings that an zone where no growth defect FPD exist between a ring OSF circumference part and LEP zone of its outer side, and proposed extending the zone throughout a wafer.

However, it is not clarified about the oxygen precipitate behavior in this zone.

#### [0023]

If the transition point of excessive point defects is in this defect-free zone, a zone of excessive atomic vacancies will exist in this defect-free zone.

The precipitated amount of oxygen may become unusually high.

It is because the precipitated amount of oxygen is dependent on excessive atomic vacancies and excessive interstitial-silicon-

P/G P

OSF LEP FPD

SiO<sub>2</sub> 2Oi Si V SiO<sub>2</sub> y I Oi SiV



atom concentration.

As shown in the following formula, oxygen deposit (for example, SiO2) will be promoted if an atomic-vacancy concentration becomes excessive, while it will be suppressed if an interstitial-silicon-atom concentration becomes excessive.

2xOi+y Si+zV xSiO2+(y-z-x) I Oi here is an interstitial oxygen atom.

Si is a silicon lattice atom.

V is an atomic vacancy.

I expresses an interstitial silicon atom.

X, y, and z express the concentration.

#### [0024]

This can be demonstrated qualitatively as follows.

In a silicon mother crystal, when an oxygen deposit is formed, its volume expands to about 2.25 increment.

In order to relax the lattice distortion generated thereby, the interstitial silicon atom is released.

If the atomic vacancy is excessive, since the released interstitial silicon atom is absorbed, precipitate of oxygen is promoted.

If the interstitial silicon atom is excessive, the oxygen precipitate is suppressed since the absorption of the released interstitial silicon atom may not occur.

#### [0025]

A difference in the variation in the precipitated amount of oxygen may arise between the zone where oxygen precipitate is promoted, and the zone where it is suppressed.

2.25



In other words, it is estimated that the difference of whether it is easy or hard to be influenced by a heat history arises.

From the view point of design of device process, one of things to be avoided most is that the density of oxygen deposit differs for every wafer.

It is required that the density of oxygen deposit does not vary between wafers.

#### [0026]

This invention was made in view of the above problems.

It aims at providing the method of producing a high quality silicon single crystal which has no growth defect in the wafer whole region, and a slight variation in the precipitated amount of oxygen, using pulling-up-speed P which is a variable having commonality and generality as a variable, by finding an optimum zone by clarifying the transition point of excessive pointdefect zone, and the transition point of the formation zone of the ring OSF and a growth defect, and by pulling up a crystal, controlling the pulling-up speed within the range of the pulling-up speed corresponding to the zone, and the silicon single crystal and the siliconsingle-crystal wafer which are produced by the method.

[0027]

#### [SOLUTION OF THE INVENTION]

In order to attain the above objective, the invention indicated in Claim 1 of this invention

P OSF



is the production of the silicon single crystal characterized by growing the crystal in the zone where an interstitial silicon atom is excessive but no aggregate exist, in growing the silicon single crystal by the Czochralski method.

#### [0028]

If it is made to thus grow the crystal in zone in which an interstitial silicon atom is excessive but no aggregate exist when growing the silicon single crystal, an interstitial silicon atom is contained excessively in the whole region of a silicon single crystal.

However, the silicon single crystal which does not include the abnormal oxygen precipitate zone resulting from a excessive atomic vacancy, or contain the growth defect which is the aggregate of an atomic vacancy, the aggregate of an interstitial silicon atom, and the crystal defect to serve as the nucleus of the oxidation induction lamination defect formed when applying a thermal-oxidation process, can be produced.

#### [0029]

Moreover, the invention indicated in Claim 2 of this invention is the production of the silicon single crystal characterized by growing the crystal controlling the crystal pulling-up speed between the transition pulling-up speed Pc at which the transition from the zone where atomic vacancy is excessive but no growth defect exists to the zone where the interstitial silicon atom is excessive but no aggregate exist occurs, and

The transition pulling-up speed Pi at which from

PcPi



the zone where the interstitial silicon atom is excessive but no aggregate exists to the zone where the aggregate of an interstitial silicon atom exists occurs, when growing the silicon single crystal by the Czochralski method,

#### [0030]

In order to grow a crystal only in the zone where the interstitial silicon atom is excessive but no aggregate exists when growing a silicon single crystal like Claim 1, it may control the factor of the temperature-gradient others of the orientation of a crystallographic axis.

However, if the silicon single crystal of this quality is grown by controlling the crystal pulling up speed like Claim 2, the silicon single crystal of desired quality can be obtained simply and reliably.

And, an uncertain simulation analysis etc. will not be needed.

#### [0031]

In this case, as indicated in Claim 3, in the case that a transition point from the zone where the atomic vacancy is excessive but no growth defect exists to the zone where the interstitial silicon atom is excessive but no aggregate exists, varies with the radial direction of a crystal, it needs to grow the crystal, controlling the crystal pulling-up speed

Between the smallest transition pulling-up speed (Pc.min) in the transition pulling-up speeds corresponding to the transition point and the largest transition pulling-up speed (Pi.max) in the transition pulling-up speeds corresponding to the transition point from the

Pc.minPi.max



zone where an interstitial silicon atom is excessive but no aggregate exists to the zone where the aggregate of an interstitial silicon atom exists.

#### [0032]

The transition point from the zone where an atomic vacancy is excessive but no growth defect exists to the zone where an interstitial silicon atom is excessive but no aggregate exists usually varies with the radial direction of a crystal in many cases.

In such a case, a whole surface cannot be made a desired defect-free zone when making a wafer, unless the crystal was grown, controlling the crystal pulling-up speed between the above Pc.min and Pi.maxes.

#### [0033]

And as indicated in Claim 4, in the case where the transition point from the zone where an atomic vacancy is excessive but no growth defect exists to the zone where the interstitial silicon atom is excessive but no aggregate exists varies with the radial direction of a crystal, the proportion of the difference between the largest transition pulling-up speed (Pc.max) in the transition pulling-up speed corresponding to the transition point, and the smallest transition pulling-up speed (Pc.min) based on Pc.min is made 0% - 7%.

Moreover, as indicated in Claim 5, the proportion of the difference between the maximum Gmax of radial direction of crystal growth temperature-gradient-in-axial-direction G just over the boundary-surface of a silicon

Pc.minPi.max

Pc.maxPc.minPc.minG
GmaxGminGmin20



melt solution and a crystal, and the minimumvalue Gmin based on Gmin is made 20% or less.

#### [0034]

Pc.maxPc.minGmaxGmin

When a transition point thus varies with the radial direction of a crystal, by setting the conditions above of Pc.max and Pc.min, or the conditions of Gmax and Gmin, the pulling-up speed for pulling up the crystal of a desired quality of only the zone where the interstitial silicon atom is excessive but no aggregate exists can be controlled.

#### [0035]

PcPiPc.maxPc.minPi.max

And, in this invention, as indicated in Claim 6, the concrete value of Pc, Pi and Pc.max, Pc.min, and Pi.max is made to determine, as indicated in Claim 6, by growing the crystal, reducing pulling-up speed reduce gradually during pulling up a single crystal performed beforehand, cutting out the sample which cuts longitudinally in parallel to the crystal growth axial direction from the grown single-crystal stick through the crystal center shaft, applying an etching process in order to remove a surface process distortion, and finding the distribution of the defect in a sample, carrying out the oxygen precipitate heat treatment, or by measuring the lifetime of a small amount of carrier, and finding the distribution of the lifetime in a sample.

#### [0036]

PcPiPc.maxPc.minPi.max

According to such a method, in principle in the pulling-up machine of any heat-retention



structure in the furnace, Pc, Pi and Pc.max, Pc.min, and Pi.max can be determined simply and correctly.

And, neither a complicated calculation, nor the simulation based on an indefinite element and an inaccurate premise is needed entirely. If pulling-up speed is controlled according to the obtained value and the crystal is grown, the crystal of desired quality can be obtained reliably.

#### [0037]

Therefore, the silicon single crystal (Claim 7) which has the quality of only the zone where the interstitial silicon atom is excessive but no aggregate exists can be obtained efficiently by the method of this invention.

The silicon-single-crystal wafer (Claim 8) obtained from this silicon single crystal contains an interstitial silicon atom excessively in the wafer whole region like Claim 9.

It becomes the silicon-single-crystal wafer which does not include the abnormal oxygen precipitate zone resulting from a surplus atomic vacancy, nor contain the growth defect which is the aggregate of an atomic vacancy, the aggregate of an interstitial silicon atom, and the crystal defect which serves as the nucleus of the oxidation induction lamination defect formed when performing a thermal-oxidation process.

#### [0038]

OSF mm/min/cm HNO<sub>3</sub>

Hereafter, this invention is demonstrated in further detail.

In this invention, the transition point of the kind



of point defect to the crystal pulling up speed, the transition point of a growth defect zone, and the transition point of a ring OSF zone are first determined as follows.

That is, the crystal is grown, fixing the variation (gamma) (mm/min/cm) of the pulling-up speed per unit length in pulling up a crystal, and reducing pulling-up speed gradually.

The sample which is cut longitudinally in parallel with the crystal growth axial direction through the crystal center shaft, is produced.

In order to remove the process distortion introduced at the time of cutting, this sample is immersed in the mixed-acid solution which consists of hydrofluoric acid (HF) and nitric acid (HNO3).

Next, the deposition of oxygen and heat treatment is given to a sample.

The analysis by the X-ray topograph method is performed.

A distribution of the defect in a sample is investigated. Or, by conducting the measurement by the lifetime method in a small amount of a carrier, and investigating a distribution of the lifetime in a sample, each transition point can be determined from a distribution diagram.

#### [0039]

The variation of the pulling-up speed per unit length was fixed, and the pulling-up speed was reduced gradually in the above-mentioned method.

However, it is not necessarily a required requirement to fix the variation.

However, when making the variation fixed, it is



convenient to evaluate relatively the crystal grown under each condition.

#### [0040]

FPD OSF FPD LEP FPD LEP LEP LEP

One example of the defective distribution diagram thus obtained is shown in Diagram 2.

Zone A is a zone where the growth defect FPD is formed.

This can be confirmed by applying seco etching to the sample to which the deposition of oxygen and heat treatment is not given, in the abovementioned samples, and by observing the surface.

Zone B is a zone where a ring OSF is formed.

Zone C is a defect-free zone in the zone where FPD and LEP of a growth defect are not observed.

However, it is the zone where oxygen precipitate occurs.

Zone D is also a defect-free zone in the zone in which FPD and LEP of a growth defect are not observed.

However, oxygen precipitate is the zone which hardly occurs (desired quality zone of this invention).

Zone E is a zone which LEP begins to form.

The oxygen precipitate has occurred slightly.

Zone F is a zone where LEP of a growth defect is observed.

It is the zone where oxygen precipitate hardly occurs.

#### [0041]

Comparing the strength of the contrast of a X-ray topograph image, and the size of the lifetime of a small amount of carrier in each



zone, if the size of the precipitated amount of oxygen is compared, it will become zone C, zone A, zone E, zone B, and zones D and F in the size order.

As mentioned above, since oxygen precipitate is suppressed when an interstitial silicon atom becomes excessive, it can judge that zones D, E and F where the oxygen precipitate was suppressed are the zone where an interstitial silicon atom is excessive.

A zone where an interstitial-silicon-atom is excessive and a zone where an atomic-vacancy is excessive, therefore, exist in a defect-free zone.

The boundary can be judged from a measurement of the difference in the precipitated amount of oxygen, or the lifetime of a amount small of carrier.

In the production of this invention, it thus finds a defective distribution diagram first, and each pulling-up-speed factor is known.

#### [0042]

Next, the production of the silicon single crystal of this invention and the silicon single crystal obtained from now on, and a silicon-single-crystal wafer are explained in full detail.

About many samples produced at the pullingup speed equivalent to zone C and zone D of the defective-free zone shown in Diagram 2, if the precipitated amount of oxygen is investigated, it will be as shown in Diagram 3.

As for the oxygen precipitate of zone C shown with a circle, the variation is also large while there are a large amount of precipitate.

As for the oxygen precipitate of zone D shown

(C) DERWENT



by the black circle, the variation is also small while the precipitate is suppressed and the amount of precipitate is small.

The ideal behavior that the amount of precipitate is mostly determined only by the initial oxygen concentration is shown.

#### [0043]

Therefore, in this invention, if a crystal is pulled up within the range of this zone D, the silicon single crystal of request quality and a siliconsingle-crystal wafer can be obtained.

That is, it is the silicon single crystal and the silicon-single-crystal wafer which are grown by a Czochralski method.

In the whole region, an interstitial silicon atom is contained excessively.

The silicon single crystal and the siliconsingle-crystal wafer which do not include the abnormal oxygen precipitate zone resulting from a excessive atomic vacancy, nor contain the growth defect which is the aggregate of an atomic vacancy, the aggregate of an interstitial silicon atom, and the crystal defect which serves as the nucleus of the oxidation induction lamination defect formed when performing a thermal-oxidation process, are actualized.

#### [0044]

If this is said by pulling-up speed, in Diagram 2, the transition from the zone where the atomic vacancy is excessive but no growth defect exists, i.e., the abnormal oxygen precipitate zone to the zone where the interstitial silicon atom is excessive but no aggregate exists, will occur at the boundary of zone C and zone D,

PcPi



and the pulling-up speed at that time will be set at Pc.

The transition from the zone where the interstitial silicon atom is excessive but no aggregate exists to the zone where the aggregate of an interstitial silicon atom exists occurs at the boundary of zone D and zone E, and the pulling-up speed at that time is set at Pi.

#### [0045]

Then, the silicon single crystal and the siliconsingle-crystal wafer with the desired quality of only D zone of this invention can be produced by the method of growing by controlling the crystal pulling up speed, between the transition pulling-up speed Pc at which the transition from the zone which the atomic vacancy is excessive but no growth defect exists, i.e., the abnormal oxygen precipitate zone to the zone where the interstitial silicon atom is excessive but no aggregate exists, occurs, and transition pulling-up speed Pi at which the transition from the zone where the interstitial silicon atom is excessive but no aggregate of an interstitial silicon atom exists to the zone where the aggregate exists, occurs.

#### [0046]

If such operation is performed with each furnace-interior heat-retention structure, in principle in any pulling-up apparatuses and structure in the furnace, Pc and Pi are discovered, and the pulling-up speed is controlled within the range of these and crystal growth is performed.

PcPi

PcPi



The silicon single crystal and the siliconsingle-crystal wafer of this invention quality can be obtained.

And, what is sufficient is just to use what is performed with the usual pulling-up apparatus, since it is a control of pulling-up speed.

Using a special apparatus in implementation of this invention is not necessarily needed.

#### [0047]

However, it is made as shown in Diagram 2 when the heat-retention structure in the furnace is optimised.

However, the transition pulling-up speed Pc and Pi often vary in the radial direction of a crystal actually.

In things of which transition pulling-up speed varies in the radial direction of a crystal, Diagrams 4 (a), (b), and (c) showed the different example.

These have 3 kinds of different heat-retention structures in the furnace.

By the above-mentioned method, it respectively found the distribution diagram of a crystal defect, setting the crystal radius at x axis and setting the pulling-up speed at y axis.

#### [0048]

As the index which expresses the difference of the heat-retention structure in these furnaces relatively, the crystal growth temperature-gradient-in-axial-direction G of boundary-surface just over the silicon melt solution and the crystal which is found by FEMAG simulation software is used.

When the ratio of the difference (DELTA) G

PcPix y

FEMAG G GsGcG



between the value (Gs) of the crystal surface (periphery part) and the value of a crystal center (Gc) based on the smaller value in the value of the crystal center and the value on the surface of a crystal was set at (eta), it was found that the value respectively differs greatly.

0.357 0.091 0.362

#### [0049]

That is, the diagram 4 (a) is the case where the growth temperature gradient in axial direction on the surface of a crystal is larger than the growth temperature gradient in axial direction of a crystal center. It is (eta) =0.357.

Diagram 4 (b) is the case where the growth temperature gradient in axial direction on the surface of a crystal is slightly larger than the growth temperature gradient in axial direction of a crystal center. It is (eta) =0.091.

Diagram 4 (c) is the case where the growth temperature gradient in axial direction on the surface of a crystal is smaller than the growth temperature gradient in axial direction of a crystal center. It is (eta) =-0.362.

#### [0050]

From this, in the case of Diagram 4 (a), throughout the crystal radial, there is no pulling-up speed which is within the zone D.

When shown in Diagram 4 (b), in the case of (eta) is positive and small, it will approximates an ideal distribution of Diagram 2.

In the case of Diagram 4 (c), like (a), throughout the crystal radial, there is no pulling-up speed which is within zone D.

#### [0051]



Pc.minPi.max

When the transition point to the zone which does not have the aggregate although the interstitial silicon atom is excessive varies from the zone which does not have a growth defect in this way although the atomic vacancy is excessive with the radial direction of a crystal

It needs to be made to carry out the growth of the crystal, controlling between the largest transition pulling-up speed (Pi.max) in the transition pulling-up speed corresponding to the transition point to the zone where the aggregate of an interstitial silicon atom exists from the zone where the aggregate does not exist, although the smallest transition pulling-up speed (Pc.min) in the transition pulling-up speed corresponding to the transition point and the interstitial silicon atom are excessive.

[0052]

Pc.maxPc.minPc.min

And, when investigating the heat-retention structure in the furnace where provides the value of (eta) which is comparatively close to the example shown in Diagram 4 (b) in many times, in order for the pulling-up speed which is within zone D to exist throughout the crystal radial, it became clear that it needs to set the proportion based on Pc.min of the difference between the largest transition pulling-up speed (Pc.max) in the transition pulling-up speeds corresponding to the transition point and the smallest transition pulling-up speed (Pc.min) at 0% - 7%.

#### [0053]

GmaxGminGmin20

Moreover, saying the conditions where the pulling-up speed which is within zone D exists



throughout the crystal radial, by the condition of the crystal growth temperature gradient in axial direction, it became clear that it needs to set the proportion of the difference between the radial maximum Gmax of the crystal growth temperature gradient in axial direction of boundary-surface just over a silicon melt solution and a crystal, and the minimum-value Gmin based on Gmin at 20% or less.

## [0054]

That is, Diagram 5 is a diagram which expresses the result that investigated the relationship of the pulling-up-speed range DELTAP=Pc.min-Pi.max which actualizes zone D, and (eta) by reducing the pulling-up speed gradually at a fixed variation to grow the crystal in various heat-retention structures in the furnace.

From this diagram, it turns out that whether (eta) is positive or a negative, DELTAP is made 0 if it is not 20% or less.

#### [0055]

And, if it pulls up, controlling pulling-up-speed P between Pc and Pi or between Pc.min and Pi.max throughout the crystal full length during crystal growth, the whole of one single-crystal stick can be made the crystal of only the zone of this invention where the interstitial silicon atom is excessive but no aggregate exists.

#### [0056]

As for the silicon single crystal thus obtained and the silicon-single-crystal wafer of this invention the interstitial silicon atom contains

P Pc.min Pi.maxP

P PcPiPc.minPi.max



excessively in the whole region. The abnormal oxygen precipitate resulting from a excessive atomic vacancy does not occur.

The oxygen precipitate behavior in which the precipitated amount of oxygen by heat treating is determined only by the initial oxygen concentration is shown.

Therefore, since the precipitated amount of oxygen formed at the heat-treating process of a device process can be determined by specifying the initial oxygen concentration, variation in the precipitated amount of oxygen can be reduced.

Moreover, since the wafer in which oxygen precipitate occurs too much is not included, design of a device thermal process becomes easy.

#### [0057]

In addition, since the nucleus of the growth defect and oxidation induction lamination defect of FPD which is an aggregate of an atomic vacancy, or LEP (the transition loop and its cluster are considered) which is the aggregate of an interstitial silicon atom is not included, the poor joining leak of a device and the poor withstand-pressure of an oxide film are reduced.

Naturally, since it is easy to control the precipitated amount of oxygen, excessive oxygen precipitate can be eliminated.

It can reduce the poor joining leak and the poor oxide-film withstand-pressure which are resulted from an oxygen deposit.

[0058]

FPD LEP



FPD COP LEP

Incidentally, in order to dissolve oxygen deposit near the surface layer, high-temperature process may be performed in a hydrogen atmosphere.

However, since it is at a high temperature, the thermal stress more than a critical shear stress is applied to a wafer, and the transition of a slip is formed.

Moreover, the metal pollution from the member in a heat-treat furnace occurs, and the yield is low and there is a problem in productivity.

By high -temperature process in hydrogen atmosphere, the growth defect FPD (called COP) disappears again only by a depth of a few microns from the surface.

And, the growth defect LEP does not disappear in the surface layer by this hydrogen heat treating.

The wafer of this invention has, therefore, higher quality than the wafer to which such high -temperature process in a hydrogen atmosphere is applied.

## [0059]

On the one hand, in this invention, the oxygen precipitate nucleus in the grown crystal is in a comparatively small amount and the oxygen precipitate by subsequent heat treating is also suppressed. It may be considered to be unsuitable for the intrinsic gettering method using oxygen deposit.

However, at the wafer production process, it is known well generally that heat treating will be performed at a low temperature of 650 degree-C etc. in order to eliminate the oxygen donor

650 650



formed during crystal cooling.

By adjusting the duration at this time, since the precipitated amount of oxygen required in a device thermal process can be adjusted, it does not become a problem at all.

The device process in recent years is made more clean. The required precipitated amount of oxygen is also reduced.

And, when determining the heat-treating duration at 650-degree C, if it is the wafer of this invention, the variation in the precipitated amount of oxygen is small. It is, therefore, effective that the heat-treating duration is set up uniquely if even the initial oxygen concentration is measured.

## [0060]

Pi.maxGsGcmin GsGcP GcGs

PcPiPc.maxPc.min, Pi.max, Since it may not need to use the temperature-Pi.minP Pc.min Pi.maxP Pc.min gradient G which is provided with different values depending on the analysing organization in the production of the silicon single crystal of this invention, there are commonality and generality.

> That is, pulling-up speed is reduced gradually, the crystal is grown, and a crystal radial position and the defective distribution to pullingup speed are investigated. If Pc, Pi, Pc.max, Pc.min, Pi.max, Pi.min, etc. are calculated, the relative comparison of this can be carried out simply.

> Also to the pulling-up apparatus to be designed heat-retention completely newly and the structure in the furnace, pulling-up speed is reduced gradually similarly, and the crystal is grown.

A crystal radial position and the defective



distribution to pulling-up speed are investigated. Therefore, whether or not the apparatus to manufacture of the silicon single crystal of this invention and the heat-retention structure in the furnace is adapted can be judged by the amount DELTAP=Pc.min-Pi.max.

Moreover, as shown in Diagram 5, from the relationship of DELTAP=Pc.min-Pi.max and (eta)= (Gs-Gc)/min {Gs, Gc}, whether it should enlarge Gc or Gs, or should be made small in order to enlarge DELTAP can be judged.

It becomes easy to design a more ideal pulling-up apparatus and the heat-retention structure in the furnace.

## [0061]

P PcPiPc.minPi.maxG P/G G P

Generally, the silicon single crystal of this invention can be produced by fixing pulling-up-speed P between Pc, Pi or Pc.min, and Pi.max with crystal growth, or making it small gradually throughout a crystal full length.

This is considered to have the relationship that the growth axial-direction boundary-surface just-over temperature-gradient G becomes fixed since a crystal seldom get cold according to crystal growth, or the parameters P/G in the above-mentioned theory proposed by Voronkov become almost fixed since it become relatively small. That is, since temperature-gradient G is fixed or becomes small according to crystal growth, it is considered that pulling-up-speed P also needs to be fixed with crystal growth, or be gradually made small.

(C) DERWENT

#### [0062]



## [Embodiment]

Hereafter, an Example is given and the embodiment of this invention is demonstrated.

However, this invention is not limited to these.

[0063]

## [Example]

The Example of this invention is demonstrated below.

First, Diagram 6 demonstrates the example of constitution of the single crystal drawing apparatus by the CZ process used in this Example.

As shown in Diagram 6, this single crystal drawing apparatus 30 is constituted by being equipped with a pulling-up chamber 31, a crucible 32 provided in the pulling-up chamber 31, a heater 34 distributed around the crucible 32, a crucible holding shaft 33 which rotates a crucible 32 and its rotating mechanism (not shown), a seed chuck 6 holding the seed crystal 5 of silicon, a cable 7 which pulls up the seed chuck 6, and a winding mechanism which rotates or winds the cable 7 up (not shown).

As for the crucible 32, a quartz crucible is provided at the side which accommodates silicon melt solution (hot water) 2 of the inner side, and the graphite crucible is provided at the outer side.

Moreover, the heat insulating material 35 is distributed around the outer side of the heater 34.



## [0064]

Moreover, in order to satisfy the manufacture conditions in connection with the production of this invention, the cyclic solid-liquid boundary-surface heat insulating material 8 is provided in the periphery of the solid-liquid boundary surface of a crystal at the bottom end of the rectification tube 9.

This solid-liquid boundary-surface heat insulating material 8 is installed at 3-10-cm intervals 10 between the lower end and the hotwater surface 3 of the silicon melt solution 2.

Moreover, the magnet 36 which impresses a magnetic field to silicon melt solution, and suppresses the convection current is distributed at the horizontal outer side of the pulling-up chamber 31.

#### [0065]

A quartz crucible with a diameter of 22 inches is filled with 110kg of silicon polycrystal raw materials using an apparatus as shown in the above diagram 6.

It energizes the graphite heater which was installed at the outside of the quartz crucible.

The silicon raw material was melted.

The distance between the lower end of the solid-liquid boundary-surface heat insulating material 8 and the hotwater surface 3 of the silicon melt solution 2 which are installed the upper of silicon melt-solution for the radiantheat shield to a crystal and for the gas rectification was set at 5 cm.

#### [0066]

And, the end of the seed crystal 5 of a silicon

110kg

200 mm



single crystal is immersed in a silicon melt solution.

It is a pulling up a seed crystal after making it get familiarized gradually. The site called neck part which is connected a seed crystal is produced. Subsequently its diameter extended gradually. Increase of its diameter is stopped when becoming a desired diameter.

It was grown at a fixed diameter.

The desired diameter at this time was set at 200 mm.

## [0067]

FEMAG GsGcmin GsGc0.093

0.7 mm/min0.005 mm/min/cm P When it became predetermined straight-barrel length, pulling-up-speed P was lowered gradually from 0.7 mm/min, at a variation (gamma) of the pulling-up speed per unit length of 0.005 mm / min/cm.

> During crystal growth, the quartz crucible was gradually pushed up so that the interval of melt solution and the solid-liquid boundary-surface heat insulating material 8 might be kept constant.

> Moreover, in order to restrain the temperature fluctuation by the melt-solution convection current and to suppress the fluctuation of pulling-up speed, the horizontal magnetic field of 4000G was impressed during a growth.

> About the heat-retention structure in the furnace at this time, the temperature gradient of the melt-solution just-over growth axial direction found by the heat-transfer analysis by FEMAG is the largest on the crystal surface.

It is the smallest at a crystal center.

The value of (eta) = (Gs-Gc)/min {Gs, Gc} was 0.093.



## [0068]

800 / 4 h (N<sub>2</sub>)1000/ 16 h (O<sub>2</sub>)

2 mm<sup>2</sup> HFHNO<sub>3</sub>30FPD LEP Two samples with a thickness of 2 mm were cut out at the diameter position in parallel with the crystal growth axis after crystal growth.

> This sample is immersed in the mixed-acid solution which consists of a hydrofluoric acid (HF) and nitric acid (HNO3).

> The process distortion introduced at the time of a cutting was removed.

> And, as for one sheet, the corrosion of the growth defect is carried out by giving minutes of the selective etching by secoetching.

> The density of FPD (aggregate of the atomic vacancy) and LEP (aggregate of the interstitial silicon atom) of a growth defect was examined.

> About the other sheet, the precipitation heat treatment of 800 degree C / 4h(N2)+1000 degree C / 16h (O2)) was given.

> There are various sequences about a precipitation heat treatment.

> However, this sequence is the most suitable, in order to grow it up by keeping the density of the oxygen precipitate nucleus contained in a grown crystal.

> The lifetime of a small amount of carrier was investigated after this precipitation treatment, and X-ray topograph photography was performed.

## [0069]

FPD OSF LEP

The defective distribution diagram obtained from the strength of the contrast of the X-ray topograph corresponding to the zone of a defect and the height of the precipitated



amount of oxygen is shown in Diagram 7.

In Diagram 7, an vertical axis expresses the position of a crystal-growth axial direction, in other words the pulling-up speed which corresponds to the position.

A horizontal axis expresses the radial position of a crystal.

Zone A is the zone of the growth defect FPD. Zone B is the zone of a ring OSF. Zone C is the zone which is has a high precipitated amount of oxygen. Zone D is the zone which is defect-free and has a low precipitated amount of oxygen (this invention quality zone). Zone E is a zone where oxygen precipitate occurs slightly. Zone F is the zone of the growth defect LEP.

#### [0070]

The measurement result of a lifetime was also written together in Diagram 7.

However, the lifetime of zone C is the lowest reflecting the existence of high density oxygen deposit.

On the one hand, in zone D, the lifetime is the highest reflecting that it is defect-free and that a formation of oxygen deposit is suppressed.

# [0071]

FPD Pc.minPi.maxPi.max
Pc.min = 0.504 mm/min Pi.max = 0.488 mm/min Pc = 0.510 mm/min

From this diagram 7, Pc.min corresponding to the point of appearing latest can be found in the boundary between zone C and zone D, i.e., boundary between the zone where the atomic vacancy is excessive but no growth defect FPD exists, and the zone where the interstitial silicon atom is excessive but no aggregate exists.

Moreover, Pi.max corresponding to the point of appearing earliest can be found in the



boundary between zone D and zone F, i.e., the boundary equivalent to zone E.

In this case, Pi.max is the value in an incrystal centre part.

The definite value thus calculated respectively as follows. Pc.min =0.504 mm/min, Pi.max = 0.488 mm/min, Pc = 0.510 mm/min.

## [0072]

0.488 mm/min OSF

Pc.min = 0.504 mm/min Pi.max = Next, in the same pulling-up apparatus as above, and the heat-retention structure in the furnace, the crystal was grown, controlling the pulling-up speed between Pc.min =0.504 mm/min which was obtained above, and Pi.max=0.488 mm/mins.

> When investigating the growth defect of the produced crystal like the above, it was confirmed that the whole region of the crystal straight barrel by which the pulling-up speed was controlled is zone D where it is defect-free without the nucleus of the growth defect and the ring OSF and the oxygen precipitate was suppressed.

> The precipitated amount of oxygen of the sample collected from this crystal is shown by the black circle of Diagram 3.

## [0073]

In addition, this invention is not limited to an above embodiment.

An above embodiment is an illustration.

Anything which has the substantially same constitution as the technical thought indicated by the claim of this invention, and has a similar effect is included in the technical range of this



invention.

## [0074]

For example, in the above embodiment, the case where the silicon single crystal with a diameter of 8 inches was grown, is demonstrated, referring to the example.

However, this invention is applicable irrespective of the diameter of the crystal to pull up.

Also, in growing of the silicon single crystal of a diameter of 6 inches or less, a diameter of 8-16 inches, or more, it is applicable.

It is needless to say that it is effective.

## [0075]

Moreover, if the control of pulling-up speed is made, this invention can be applied to any kind of pulling-up apparatus and an apparatus of the structure in the furnace.

The existence of impression of the magnetic field to silicon melt solution is not asked, either.

Moreover, the magnetic field impressed when impressing a magnetic field is not restricted to a horizontal magnetic field. When impressing the so-called longitudinal magnetic field, a cusp magnetic field, etc., it can apply.

Moreover, in order to produce the crystal of only D zone which is this invention quality, not only the pulling-up speed is controlled, but also it may control the temperature-gradient G in the crystal or the other factor.

This invention does not eliminate the case where such a control is carried out.

## [0076]

G



FPD COP

04/17/00

## [EFFECT OF THE INVENTION]

As demonstrated above, the silicon single crystal and the silicon-single-crystal wafer of this invention do not include the nucleus of the growth defect (the cavity called FPD and COP, the transition loop, and its cluster) which is the aggregate of the point defect formed during crystal cooling, and the oxidation induction lamination defect over the whole region.

Therefore, a poor oxide-film withstand-pressure and poor joining leak are reduced.

In addition, since the interstitial silicon atom is excessive in the whole region, abnormality (high density) oxygen precipitate does not occur. Consequently, there is no variation in the precipitated amount of oxygen between wafers, and design of a device thermal process becomes easy.

And also since high density oxygen deposit may not occur, the poor joining leak resulting from it does not occur.

Therefore, it contributes to the improvement in the production yield of the highly integrated semiconductor device.

Moreover, in the production of the silicon crystal of this invention, single the implementation conditions of the silicon single crystal of this invention is regulated only by pulling-up speed without using the value of temperature-gradient G calculated from a simulation. Consequently, there are commonality and generality in the production of the silicon single crystal of this invention.

There is the feature that it can utilize widely



and it contributes to industrial production greatly.

## [BRIEF EXPLANATION OF DRAWINGS]

OSF LEP

## [FIGURE 1]

It is the sketch diagram of the data which show the existence of a defect-free zone between a ring OSF zone and LEP (transition loop and its cluster) zone.

## [FIGURE 2]

About the crystal grown by reducing pulling-up speed gradually at a fixed variation, it is an example diagram describing the defective distribution by making the crystal radial position as a horizontal axis, and the pulling-up speed (position of a crystal straight body part) as the vertical axis.

# [FIGURE 3]

It is the diagram having shown the oxygen precipitate behavior of the sample collected from the crystal grown at the pulling-up speed which adapts zone C and zone D among the defect-free zones shown in Diagram 2.

Zone C is expressed with a circle and zone D are expressed with a black circle.

# [FIGURE 4]

About the crystal grown by reducing pulling-up speed gradually at a fixed variation, in 3 kinds of heat-retention structure in the furnace, it is a diagram describing the defective distribution making the crystal radial position as the



horizontal axis and the pulling-up speed (position of a crystal straight body part) as the vertical axis.

(a) is the case where the growth temperature gradient in axial direction on the surface of a crystal is larger than the growth temperature gradient in axial direction of a crystal center. (b) is the case where the growth temperature gradient in axial direction on the surface of a crystal is slightly larger than the growth temperature gradient in axial direction of a crystal center. (c) is the case where the growth temperature gradient in axial direction on the surface of a crystal is smaller than the growth temperature gradient in axial direction of a crystal center.

#### P Pc.min Pi.max

## [FIGURE 5]

In various heat-retention structures in the furnace, the crystal is grown by reducing pulling-up speed gradually at the fixed variation. It is a diagram showing the result investigated the relationship of pulling-up-speed range DELTAP=Pc.min-Pi.max which actualizes zone D of Diagram 2, and (eta).

## [FIGURE 6]

It is the example figure of constitution of the single crystal drawing apparatus by the CZ process used in the Example.

## [FIGURE 7]

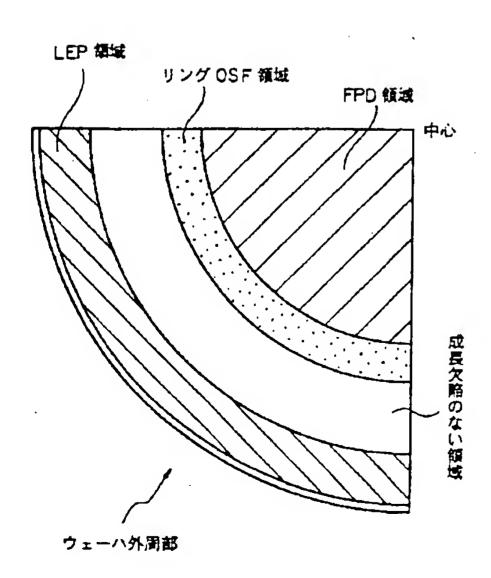
It is the defective distribution diagram and the value of the lifetime which were obtained in the Example.



# [EXPLANATION OF DRAWING]

1... growth single-crystal stick, 2... silicon melt solution, 3... hotwater surface, 4... solid-liquid boundary surface, 5... seed crystal, 6... seed chuck, 7... cable, 8... solid-liquid boundary-surface heat insulating material, 9... rectification tube, 10... The clearance between a hotwater surface and a solid-liquid boundary-surface heat-insulating-material lower end, 30... A single crystal drawing apparatus, 31... pulling-up chamber, 32... crucible, 33... crucible holding shaft, 34... heater, 35... heat insulating material, 36... magnet.

## [FIGURE 1]

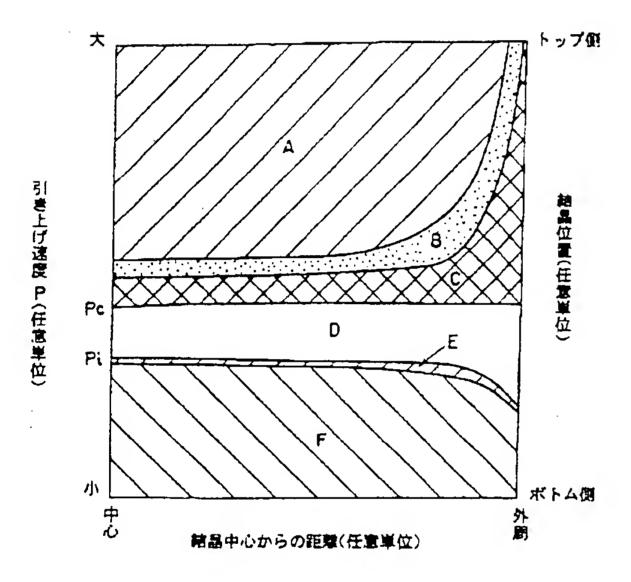


LEP zone, Ring OSF zone, FPD zone, the center, A zone where no growth



defect exists, Wafer periphery

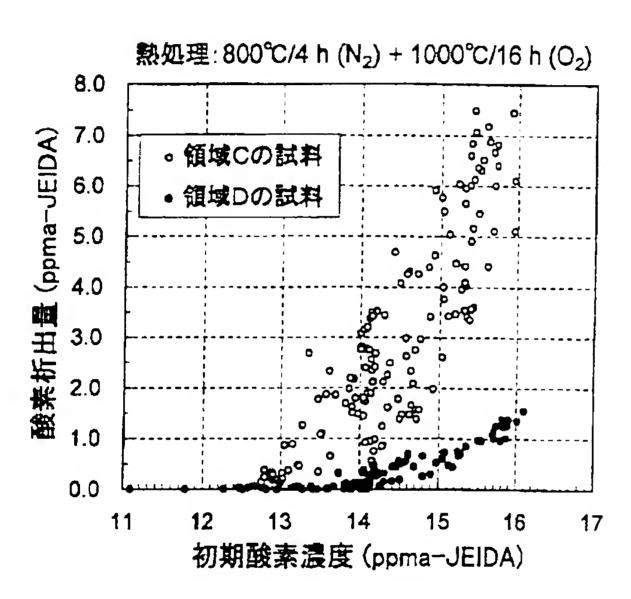
# [FIGURE 2]



Vertical axis (left): Pulling up speed P (arbitrary unit), High, low, Vertical axis (right): Crystal position (arbitrary unit), Top side, bottom side, Horizontal axis: The distance from the crystal center, the center, periphery



# [FIGURE 3]



#### Heat treatment

Vertical axis: the oxygen precipitate amount

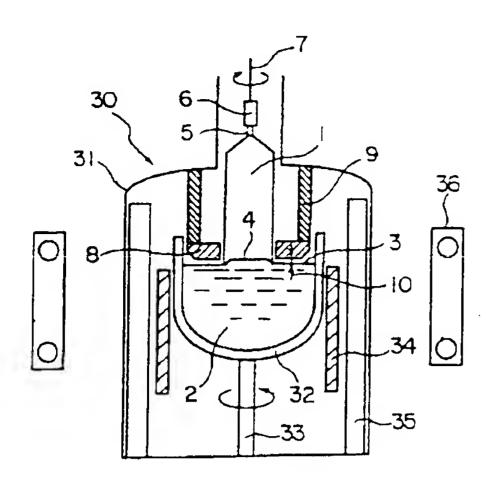
Horizontal axis: the initial oxygen concentration,

a circle: the sample of zone C

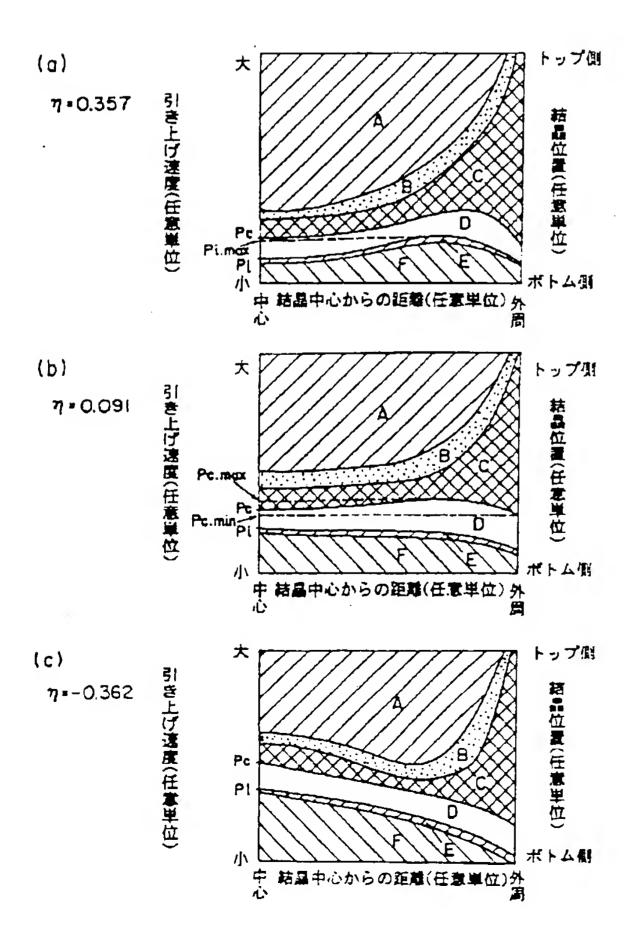
a black circle: the sample of zone D

# [FIGURE 6]





# [FIGURE 4]





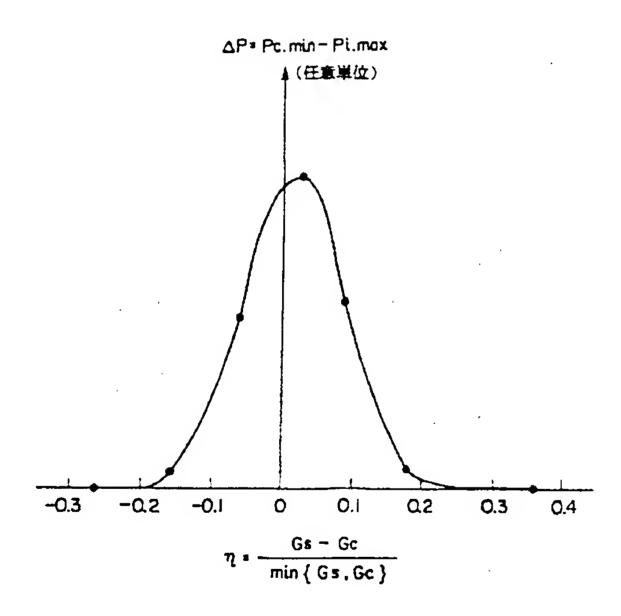
(a), (b), (c)

Vertical axis (left): Pulling up speed (arbitrary unit), High, low,

Vertical axis (right): Crystal position (arbitrary unit), Top side, bottom side,

Horizontal axis: The distance from the crystal center, the center, periphery

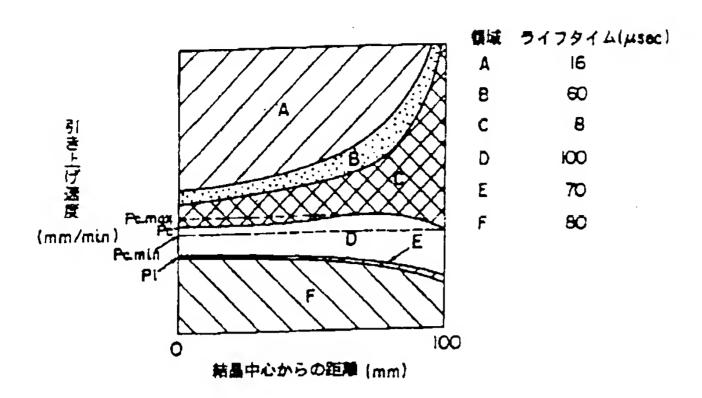
# [FIGURE 5]



(arbitrary unit)

[FIGURE 7]





Vertical axis (left): Pulling up speed P (arbitrary unit) Horizontal axis: The distance from the crystal center Zone A-F, Life time



# **DERWENT TERMS AND CONDITIONS**

Derwent shall not in any circumstances be liable or responsible for the completeness or accuracy of any Derwent translation and will not be liable for any direct, indirect, consequential or economic loss or loss of profit resulting directly or indirectly from the use of any translation by any customer.

Derwent Information Ltd. is part of The Thomson Corporation

Please visit our home page:

"WWW.DERWENT.CO.UK" (English)

"WWW.DERWENT.CO.JP" (Japanese)